Internal Cyclization during Dediazoniation of 2,5-Bis(1,1,2,2-tetramethylpropyl)benzenediazonium Ion

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The synthesis of 2-amino-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (1) was recently published. It has been reported that thermal decomposition of ortho-alkylbenzenediazonium ions can result in internal ring closure reactions. Thus the thermal decomposition of the diazonium ion derived from 1 has now been studied.

A product composition consisting of 93% of 1,1,2,2-tetramethyl-5,1',1',2',2'-tetramethylpropyldiine (2) and 7% of 2-hydroxy-1,4-bis(1,1,2,2-tetramethylpropyl)benzene (3) was obtained when the diazonium ion derived from 1 was thermally decomposed in 3 N sulfuric acid. In order to make a comparison with and confirm previous results, those experiments were repeated under the present experimental conditions. The results are presented in Table 1. The formation of 13% of indane and 35% of 2-methylindane from ortho-propylaniline and ortho-isobutylaniline, respectively, along with the corresponding phenols was confirmed. Ortho-neopentylaniline was shown to give 83% of 2,2-dimethylindane and 17% of ortho-neopentylphenol. Since ortho-neopentylphenol was not isolated in the previous study, its structure was established by its mass and 1H NMR spectrum. The difference in product composition from the earlier report on the thermal decomposition of ortho-neopentylbenzenediazonium ion in 18 N sulfuric acid

In dediazoniations of ortho-alkylsubstituted diazonium ions steric bulk of the alkyl groups clearly plays an important role in the product-forming step. The bulkiness of the 1,1,2,2-tetramethylpropyl (tripyl) group in electrophilic aromatic substitutions has been demonstrated, and it is also shown in nucleophilic substitution, as it clearly yields less phenolic product (Table 1) in dediazoniation of the corresponding diazonium ion than does ortho-neopentylamine.

In a report regarding dediazoniation of the diazonium ion from 3-amino-4-tert-butyl-5-nitrobenzoic acid, ring closure yielding a benzoxylobutene derivative was found. As it can be viewed as a substituted ortho-tert-butylbenzene derivative a careful search was made in order to detect any benzoxylobutene derivative but none was found. The only minor product (less than 1%) formed in the thermolysis of 1 had a mass spectrum with a nominal mass incompatible with a benzoxylobutene derivative. 1H NMR spectroscopic studies of the 1,4-bis(1,1,2,2-tetramethylpropyl)benzene system have been discussed under the assumption that in the favoured conformation the triptyl groups are perpendicular to the aromatic ring. This means that the α-methyl groups are not in the most favoured conformation for ring closure to a benzoxylobutene derivative. Knight et al. observed in their system the buttressing effect of the 5-nitro group was necessary to get ring formation. The nitro group probably increases the population of a conformation with one of the α-methyl groups in the ring plane close to the diazonium group.

The thermal decomposition of arene-diazonium ions in acidic aqueous solution is now generally believed to proceed by heterolysis with formation of phenyl cations. The absence of any considerable amounts of by-products (Table 1) in the thermolysis of ortho-alkylsubstituted benzene diazonium ions strongly indicates that intramolecular cyclization does not occur via the formation of a primary aliphatic carbocation by a 1,5-hydride ion shift from a β-methyl group on the side chain of the initially formed phenyl cation. Such 1,5-hydrogen shifts are known to occur in compounds where resonance stabilization is involved. Also, in the special case of benzylic hydrogens the formation of a so-called penta-coordinated carbocation is discussed. A similar type of intramolecular cyclization has been reported in the acid catalyzed cleavage of 2,4,6-tri-tert-butylbenzyl methyl ether. Moreover, formation in the gas phase of primary aliphatic carbocations is known to be almost as difficult as formation of phenyl cations so the most relevant explanation seems to be a direct attack by a phenyl cation on the alkyl side chain.

Experimental. GLC analyses were performed with a Perkin-Elmer 3920 gas chromatograph equipped with flame ionization detectors and 2


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Table 1. Dediazoniation of o-alkylbenzenediazonium ions in 3 N sulfuric acid.

<table>
<thead>
<tr>
<th>Alkyl group</th>
<th>Product composition (%)</th>
<th>Total product yield (%)</th>
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<tbody>
<tr>
<td></td>
<td>Indane</td>
<td>Phenol</td>
</tr>
<tr>
<td>Propyl</td>
<td>13</td>
<td>87</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>Neopentyl</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>Triptyl</td>
<td>93</td>
<td>7</td>
</tr>
</tbody>
</table>

Identification of o-neopentlyphenol. Separation of o-neopentlyphenol from 2,2-dimethylindane and ortho-isobutylyphenol, showing equal responses on the particular detector used. This is also assumed to hold for the other compounds investigated. Mass spectra were recorded with an LKB 9000 instrument fitted with a gas chromatograph (at the Department of Medical Chemistry of Göteborg) using the same stationary phase and 1H NMR spectra were recorded on a Bruker WH 270 instrument operating at 270 MHz.

Diazonation and thermal decomposition. To a stirred, cooled (−5 °C) suspension of J in 6 N sulfuric acid an equimolar amount of sodium nitrite in aqueous solution was added in small portions. Stirring was continued at that temperature for 45 min whereupon the reaction mixture (a white precipitate was present during the whole reaction) was poured into boiling 3 N sulfuric acid. The mixture was boiled for 10 min, cooled, diluted with aqueous sodium chloride and extracted with ether. The remaining water phase was made alkaline and ether extracted. No starting material could be found in the latter ether extract.

After the usual work-up procedure, the remaining crystalline residue was shown by GLC to be a mixture of two compounds in a ratio of 53:7, based on normalized peak-area values. These two compounds were identified by GLC-MS as 1,1,2,2-tetramethyl-5-′,1′,2′,2′-tetramethylpropyldiene (2) and 2-hydroxy-1,4-bis(1,1,2,2-tetramethylphosphoryl)benzene (3), respectively. Recrystallization of the crude material (from methanol) yielded pure 2, m.p. 126−127 °C. MS [IP 70 eV; m/e (rel. int.):] 272(0.2), 218 (100), 214(6), 200(6), 185(16), 131(6), 91(24), 57(8), 41(11). NMR (270 MHz, CDCl₃): δ 0.83 (9H, s, tert-butyl), 0.96 (6H, s, 2,2-dimethyl), 1.07 (6H, s, 1,1-dimethyl), 1.33 (6H, s, 1′,1′-dimethyl), 2.66 (2H, s, methylene), 6.98 (1H, d, J 8.1 Hz, aromatic), 7.14 (1H, s, aromatic), 7.16 (1H, d, J 8.1 Hz, aromatic). MS of compound 3 [IP 70 eV; m/e (rel. int.):] 290(0.3), 275(2), 237(4), 174(100), 176(16), 175(11), 161(12), 149(10), 135(5), 107(5), 91(4), 57(24), 41(19).

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